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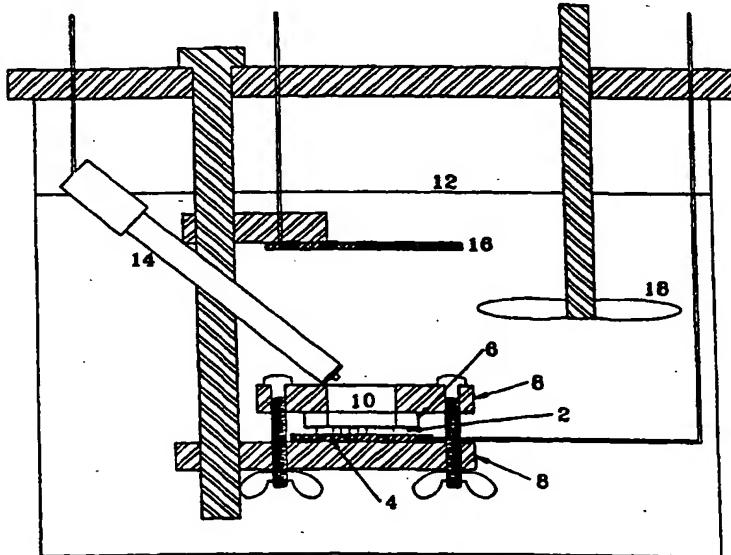
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(54) Title: HIGH ASPECT RATIO, MICROSTRUCTURE-COVERED, MACROSCOPIC SURFACES

(57) Abstract

An apparatus and method are disclosed for forming high aspect ratio microstructures ("HARMs") on planar or nonplanar surfaces, using a modification of the LIGA microfabrication process. A free-standing polymer sheet (2) is lithographically patterned with through-holes. The polymer sheet is then pressed against, clamped to, or otherwise attached to a conductive substrate (4) in such a way that the patterned holes in the sheet are not blocked. Subsequent electroplating produces well-defined HARM structures on the planar or nonplanar surface, in shapes that are complementary to the lithographically patterned through-holes in the polymer. The polymer may then be removed (e.g., by melting, dissolution, or burning). Various planar and nonplanar surfaces have been covered with microstructures (6). Where the metal surface is non-planar, the polymer sheet may be heated or otherwise made sufficiently flexible to conform to the metal surface, preferably by heat shrinking to assure firm contact. The process may be used to electroplate microstructures directly onto metal surfaces generally, not just onto metal surfaces that have been specially prepared for LIGA processes, as has previously been the case.



HIGH ASPECT RATIO, MICROSTRUCTURE-COVERED, MACROSCOPIC SURFACES

TECHNICAL FIELD

This invention pertains to macroscopic surfaces whose properties are altered by being covered with microstructures, and to an apparatus and method useful in manufacturing such surfaces.

BACKGROUND ART

The properties of many macroscopic structures depend in large part on their surface properties. For example, the rate of heat transfer between a structure and its surroundings depends on the ease with which radiative, conductive, and convective heat transfer occur between the surface of the structure and the surroundings. As another example, the strength of composite materials is often governed by the strength of the bond between the "internal" surfaces joining the different lamina. As yet another example, the rate of activity of a catalytic surface often depends on its surface area.

Efforts have been made to control the interaction of surfaces with their surroundings by painting, roughening, anodizing, hardening, plating, smoothing, and the like. In many cases, the resulting improvements in surface properties are relatively small.

One area where surface effects are important is the operation of gas turbines. The efficiency and power of a turbine increase as the maximum allowable gas inlet temperature increases. This allowable inlet temperature is a function of the composition of the turbine blades; and the balance of various modes of heat transfer into and out of the blade. Internal active cooling of turbine blades (a mode of heat removal), coupled with thermal barrier coatings on their surfaces (limiting heat transfer into the blades), allows the blades to operate at a relatively low temperature in an environment hundreds of degrees higher. A reduction in the rate at which heat is transferred from the surrounding combustion gases to the blade would allow operation at higher temperatures and efficiencies.

Both the thermal efficiency and the power output of a turbine rise as the pressure ratio and the accompanying inlet temperature increase. For example, using estimates of turbine

has used microstructures. As discussed further below, I have discovered a technique for acoustic dampening by covering a surface with microstructures.

No prior work on composite materials has used microstructures to improve bonding between layers of a composite. Prior methods of bonding laminates have generally used chemical bonding techniques. As discussed further below, I have discovered a technique for bonding layers of a laminate by using microstructures at the interface.

The LIGA process for making microstructures is well known in the art. See, e.g., E. Becker *et al.*, "Fabrication of Microstructures with High Aspect Ratios and Great Structural Heights by Synchrotron Radiation Lithography, Galvanoforming, and Plastic Moulding (LIGA Process)," *Microelectronic Engineering*, vol. 4, pp. 35-56 (1986). The conventional LIGA process combines deep-etch X-ray lithography, electrodeposition, and polymer molding. Conventional LIGA is illustrated schematically in Figures 4(a) through 4(d). As illustrated in Figure 4(a), an electrically conductive substrate 102 is glued or chemically bonded to a layer of a photoresist 104 such as polymethyl methacrylate ("PMMA") tens or hundreds of microns thick. The layer of resist is exposed to x-rays 106 through mask 108. Where mask 108 allows radiation 106 to pass, resist 104 degrades and becomes soluble in a developer. After development (Figure 4(b)) the regions on substrate 102 that are no longer covered with resist 104 serve as initiation sites to electroform metal microstructures 110 (Figure 4(c)). Following electroforming, removal of the remaining resist 104 produces a substrate covered with free-standing structures (Figure 4(d)), which may then be used as a mold insert in forming a polymeric microstructure (not illustrated).

Prior work on microstructures (those whose dimensions are smaller than about 1 mm) has focused almost entirely on "microscopic" uses of microstructures. Little consideration has been given to "macroscopic" applications of microstructures, i.e., the use of microstructures to affect the interactions between macroscopic objects and their surroundings. No prior, general methods are known for manufacturing microstructures directly onto a metal surface of interest.

a few hundred microns from the substrate surface (for example, on the surface of a turbine blade). The individual "umbrellas" in this canopy are more-or-less rigidly connected to the substrate by microposts. The canopy greatly reduces both convective and radiative heat transfer from the surrounding environment to the substrate. Particularly when used in conjunction with internal cooling of the substrate, the temperature of the substrate will be far lower than has previously been possible in otherwise similar environments. For example, as compared to prior thermal barrier coatings, when such microstructures are used to cover turbine blades the turbines can operate at substantially higher temperatures (as much as 290°C higher than otherwise possible) and substantially higher pressures, while simultaneously reducing thermal stresses. The novel barrier canopies, coupled with state-of-the-art internal cooling systems, will allow operation of turbines having inlet gas temperatures as high as 1427°C (2600°F).

An example is an article of manufacture comprising a heat barrier to reduce heat transfer between an object and the surroundings, wherein: (a) the object has a first face whose surface area is at least about 10 cm²; (b) said heat barrier comprises a plurality of at least about 10 microstructures per cm² of surface area of the first face; (c) each of said microstructures comprises a shield and a post, wherein each of said shields comprises a distal face and a proximal face, and wherein each of said posts comprises a distal end and a proximal end; (d) said distal end of said post of each of said microstructures is connected to said proximal face of said shield of said microstructure; (e) said proximal end of said post of each of said microstructures is connected to the first face of the object; (f) the surface area of the distal face of each of said shields is at least about 0.001 mm²; and (g) the distance between the proximal face of each of said shields and the first face of the object is between about 0.01 mm and about 2.0 mm; whereby total heat transfer between the object and the surroundings is substantially less than would be the heat transfer between an otherwise identical object lacking said heat barrier and the surroundings.

Preferably: said heat barrier comprises a plurality of at least about 5000 microstructures per cm² of surface area of the first face; (b) the surface area of the distal face of each of said shields is at least about 0.01 mm²; and (c) the distance between the proximal face of each of said shields and the first face of the object is between about 0.1 mm and about 1.0 mm.

In an alternative embodiment, if the "umbrellas" in the canopy are so large that they merge into one another, a continuous wall is formed that is connected to the underlying object by numerous microposts.

Preferably, adjacent microstructures are spaced between about 20 μm and about 50 μm apart from one another, the wall is at least about 0.5 mm tall in the direction perpendicular to said face, and the height of the microstructures is at least about 10 times the distance between adjacent microstructures.

The novel thermal barrier has significantly higher resistance to heat transfer than do existing film coatings such as those made of zirconium dioxide. The novel thermal barrier also greatly reduces the thermal stresses that can otherwise occur at the substrate-coating interface as a result of thermal expansion coefficient mismatch during thermal cycling.

Yet another application is the use of microstructures as acoustic absorbers, to reduce the amplitude of sound transmitted through a surface. Covering the surface with appropriate microstructures can reduce the amplitude of transmitted vibrations, and can therefore reduce the amplitude of the sound transmitted to the surrounding medium. Also, catalytic surface performance might be enhanced by the presence of microstructures on the surface due to the increase in area available for reaction.

It has been discovered that the performance of many macroscopic structures (those whose dimensions are on the order of centimeters, meters, or even larger) can be greatly improved by covering their surfaces with microstructures. In addition, a novel apparatus and method have been discovered for forming high aspect ratio microstructures ("HARMs") on planar and non-planar surfaces, using a modification of the LIGA microfabrication process. A free-standing, non-conductive sheet (e.g., a polymer or ceramic sheet) is patterned lithographically or by LIGA with through-holes. The non-conductive sheet is then pressed against, clamped to, or otherwise attached to a conductive substrate in such a way that the patterned holes in the sheet are not blocked. Subsequent electroplating produces well-defined HARM structures on the planar or non-planar surface, in shapes that are complementary to the lithographically patterned through-holes in the non-conductive sheet. The sheet may then be removed (e.g., by melting, dissolution, or burning).

Various planar and non-planar surfaces have been covered with microstructures through the new technique. Where the metal surface is non-planar, a polymer sheet may be heated or otherwise made sufficiently flexible to conform to the metal surface, preferably by heat-shrinking to assure firm contact.

The novel process may be used to electroplate microstructures directly onto metal surfaces generally -- not just onto metal surfaces that have been specially prepared for LIGA processes, as has previously been the case.

that will not remove the glue bonding the remaining high-molecular weight template to the substrate. The glue from the exposed and developed areas is then extracted with a solvent under conditions that will not significantly remove glue that is bonding the remaining high-molecular weight template to the substrate. The development of the template and the partial extraction of glue may, depending on the geometry of a particular pattern, be performed as a single step. For example, the monomer methylmethacrylate may be used as the glue. The monomer will be dissolved in the same solvent that is used to develop the exposed PMMA, but under conditions of time and temperature that will not significantly "undermine" the monomer that adheres the high molecular weight PMMA to the substrate. In a related modification, a developed template is applied in lieu of this undeveloped template, but a thin backing remains in the developed areas when the template is glued to the substrate. The thin backing is then removed, for example by chemical or radiation-induced etching. A template with such a thin backing could be formed, for example, by a molding process.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1(a) and 1(b) illustrate schematically an embodiment of a turbine blade covered with microstructures that may be manufactured through the use of the present invention.

Figure 2 illustrates a preferred geometry for microstructures used to cover a turbine blade.

Figures 3(a) and 3(b) illustrate heat flow through a surface with and without a microstructure canopy, respectively.

Figures 4(a) through 4(d) schematically illustrate the LIGA process.

Figures 5(a) and 5(b) illustrate cross sections of microstructures used in a thermal barrier covered with microstructures, that may be manufactured through the use of the present invention.

Figure 6 is a photograph of a non-conductive, self-supporting template in accordance with the present invention.

Figure 7 schematically depicts electroplating apparatus used to manufacture one embodiment of microstructures on a nickel surface in accordance with the present invention.

approximately 100°C. The exposed PMMA sheet was held above the same hot plate until it became flexible, at which point it was wrapped around the cylinder and secured with a clamp. The cylinder was removed from the hot plate and cooled to room temperature. Because the thermal expansion coefficient of PMMA is greater than that of nickel, the PMMA shrink-fit onto the nickel cylinder.

The PMMA was then developed by immersing the PMMA-coated nickel cylinder into GG developer (V. Ghica and W. Glashauer, "Verfahren für die Spannansfreie Entwicklung von Bestrahlten Polymethyl-methacrylat-Schichtyen," Offenlegungsschrift DE3039110, Siemens AG, München, Germany), producing a field of square through-holes in the PMMA. Electroplating was then used to fill the square through-holes in the PMMA with nickel. The PMMA was removed with acetone, resulting in a cylinder covered with microscopic square posts.

On a flat substrate, conventional LIGA produces structures with lateral dimensions that are constant to submicron accuracy. On a non-planar surface, the novel process can produce structures whose lateral dimensions may vary. For example, the width of the microstructures on the cylindrical shaft described above increases with the distance from the underlying substrate. However, if the radius of the cylinder is large compared to the thickness of the PMMA template used to define the shapes of the microstructures, then the distortion in the shapes of the microstructures will be minimal. For example, if the roller diameter is 5.0 cm, the nominal lateral dimension of a microstructure is 100 μm , and the thickness of the polymer template is 500 μm , then the lateral dimension of the structures will vary from 99.5 μm at the base to 100.5 μm at the top. In many applications, a deviation of this magnitude is negligible.

A HARM-covered cylinder such as that described above could be used in a rolling operation to produce HARM-covered sheet in a mass-production embossing process.

Example 3: Thermal barriers; application to turbine blades

In one embodiment, thermal barrier microstructures will be manufactured on a turbine blade. A mold insert will be manufactured to mold or emboss a pattern of microstructures into a thin film of polymer as described above. The polymer film, containing voids where structures in the mold insert were present, is applied to the blade surface. An electroplating process then fills voids in the polymer with metal, thereby building a field of microstructures

The surface of blade 2 is covered with microstructures 6 whose shape is generally as illustrated in Figure 1(b). Each microstructure comprises a rectangular column 8 oriented normal to the blade surface and capped by a rectangular plate 10. A preferred geometry for microstructures 6 is illustrated in Figure 2. Note that the length dimension of each column 8 is oriented parallel to the length of blade 2. The stresses in the microstructure reach a maximum at the base of the microstructures that are near the tip of the blade, where centripetal forces are greatest.

With a blade length of 0.3 meter and a rotational velocity of 30,000 rpm, the acceleration at the tip of the blade is $a = 2.96 \times 10^6 \text{ m}^2/\text{sec}$. The force per unit length p applied to the structure is $p = \rho hwa$, where ρ is the density of the material (for nickel, $\rho = 8000 \text{ kg/m}^3$), h is the height of the cantilever (assumed to be 500 μm), and w is the cantilever width (assumed to be 40 μm), giving a value of $p = 189 \text{ N/m}$.

The maximum moment within the cantilever beam occurs at its base. The magnitude of the moment is $M = 0.5pL^2$, where L is the length of the cantilever (assumed to be 500 μm). The moment at the base of the cantilever is $2.36 \times 10^5 \text{ N-m}$. The moment at the base of the cantilever is used to calculate the maximum stress in the beam: $\sigma_1 = Mc/I$, where σ_1 is the stress due to the distributed load of the beam, c is the distance from the neutral axis ($h/2$), and I is the moment of inertia ($h^3b/12$). The maximum stress due to the distributed load occurs at the base of the cantilever beam, and has a magnitude of $8.85 \times 10^7 \text{ N/m}^2$ ($= 12.8 \times 10^3 \text{ psi} = 12.8 \text{ ksi}$).

A similar analysis can be used to estimate the contribution of the mass on the end of the cantilever to the total stress. In this case, the moment induced at the base of the cantilever by the mass is equal to the product of the force due to that mass (i.e., the mass multiplied by the centripetal acceleration) and the length of the cantilever beam. The stress induced by the "weight" at the end of the beam is $\sigma_2 = Mc/I$. The magnitude of this second stress component is 4.3 ksi. The sum of the two components gives the maximum stress in the microstructure, approximately 17.1 ksi. This maximum stress is low enough to conclude that creep-induced deformation should not be a significant problem over reasonable operational time spans. Similarly, the maximum deflection of the end of the cantilever beam is low, and can be calculated by superposition to be less than 1.0 micron.

where σ is the Stephan-Boltzmann Constant (5.88×10^{-12} W/cm²·°K). The radiative heat flux to the blade is thus 25 W/cm², and the total heat flux across the blade ($q_{total} = q_{conv,2a} + q_{rad,2a}$) is 160 W/cm². This heat is removed by fluid forced through internal ducts within the blade. The magnitude of the heat transfer coefficient, $h_{conv,2a}$, is given by $h_{conv,2a} = q_{total}/(T_{blade} - T_{gas})$. The calculated magnitude of $h_{conv,2a}$ is then 0.40 W/cm²·°K.

Analysis with microstructure canopy. In this analysis the temperature of the blade is held at 1073°K as before, and the parameters associated with internal cooling are assumed to be the same. With the same parameters, it follows that the heat flux across the blade is the same as calculated in the previous section (160 W/cm²). This heat flux value then allows calculation of the maximum allowable turbine gas temperature and the corresponding shield temperature for the case where microstructures are present. The maximum allowable temperature of the gas and the shield is estimated by assuming radiative heat transfer to be linear, and by evaluating the relative magnitudes of the linear thermal resistances between the temperatures of interest (T_{gas} , T_{shield} , and T_{blade}). The following two additional assumptions are also made: (1) All emissivities have a value of 1.0. (2) The array of microstructures forms a radiation shield. Heat transfer between the shield and the blade occurs by conductive and radiative heat transfer only. Radiative heat transfer is calculated based on the area of the surface not occupied by the support structures (the rectangular posts in the embodiment of Figures 1 and 2). Conductive heat transfer is calculated based on the percentage of the total cross sectional area occupied by the support structure. The velocity of the gas in the space between the shield and the blade is minimal, and convective heat transfer may therefore be disregarded.

Heat transfer between the shield and the blade surface is the sum of the conductive and radiative heat transfer components:

$$q_{cond,lb} = (A_m/A_s) (K_m/L) (T_{shield} - T_{blade})$$

$$q_{rad,lb} = h_{rad,lb} (1 - A_m/A_s) (T_{shield} - T_{blade})$$

$$h_{rad,lb} = 4\sigma T_{m2}^3$$

where $T_{m2} = (T_{shield} + T_{blade})/2$; A_m = area of microstructure support (approximately 10% of total); A_s = total area of shield; K_m is the thermal conductivity of the support structure

A similar analysis shows that for a given inlet turbine gas temperature, the blade temperature will decrease 150-175°K with the microstructure canopy. The novel microstructure thermal barrier coating has tremendous potential.

Manufacture of Microstructure-Covered Blades. The manufacturing techniques described here for thermal barriers may be applied generally to other microstructure-covered surfaces as well, such as those used in augmenting heat transfer, in composite materials, and in acoustic barriers (although the use of heat-resistant materials may not be necessary in all applications). Thin sheets of polymer film will be used to manufacture large fields of HARM through holes.

Exposing a large area of resist in a single exposure (on the order of 10 cm x 10 cm) is more efficient than exposing an equal area in a series of exposures of smaller areas, because the rate of production during molding is proportional to the size of the mold. Larger mold inserts are more easily manufactured from larger regions of patterned resist. To expose such large areas of resist, the resist typically must be moved relative to the x-ray beamline. Two approaches may be used to expose large areas of resist. If the area of the mask pattern is small relative to the area of resist to be exposed, then the resist is moved with respect to the mask (or vice versa) through a series of accurately calibrated "steps" through means known in the art. On the other hand, if the area of the pattern on the mask is the same as the area of resist to be exposed, then the mask and resist can be moved in tandem relative to the beamline.

Several methods may be used to reproduce HARMS efficiently from template or mold inserts. The advantages gained by exposing a large area of resist can be significant. However, where fields of microstructures must cover areas on the order of hundreds of cm² or even m², it is impractical to manufacture the material using only a lithography electroplating process. In such cases, it may be more practical to repeatedly reproduce a relatively small pattern from a mold insert. The mold insert is used in a polymer molding process to fabricate polymer sheets containing voids where the structures were present in the insert, and vice versa. The polymer sheets are then bonded to a conductive surface (e.g., a turbine blade), and microstructures are electroplated in the voids in the polymer film. The polymer is then removed after the electroplating process is completed, e.g., by dissolution in solvent.

Above 1273°K, Cr₂O₃ may be oxidized to CrO₃, which is a volatile compound. However, the higher end of the projected service temperature range is above 1273°K. A Ni-Cr alloy may therefore not suffice in all applications. Alternative alloys for use at higher temperatures include electroformed Ni-Al binary alloy, Ni-Cr-Al ternary alloy, and Ni-Cr-Al-Y alloy. These coatings rely on a continuous Al₂O₃ scale for oxidation resistance. Such a scale is known to form on nickel aluminides, NiCrAlY, and CoCrAl coatings. The scale is an effective oxidation barrier over the temperature range 1100°K to 1400°K. Ni_xAl_{1-x} and Al-Cr may be co-deposited from non-aqueous baths. See, e.g., T. Moffat, J. Electrochem. Soc., vol. 141, pp. 3059 *ff* (1994). Co-electrodeposition of Y with the transition metals will be performed with methods analogous to those used in S. Powers *et al.*, Materials Chem. & Phys., vol. 35, pp 86 *ff*. (1993). Another alternative is to deposit individual layers of elemental metals separately, then to complete the alloying reactions by diffusion at elevated temperature.

Example 4: Prototype Manufacture

In one prototype, "mushroom" shaped canopies were manufactured 300 μm tall, with 170 x 170 μm square posts, topped by square canopies 300 to 300 μm in diameter at the base.

A 0.1 μm-thick nickel film, deposited from a modified Watts bath, adhered well to a silicon wafer. The composition of the modified Watts bath was as follows: NiSO₄ · 6H₂O (300 grams/liter), NiCl₂ · 6H₂O (45 grams/liter), boric acid (45 grams/liter), sodium lauryl sulfate (0.3-0.5 grams/liter), saccharin (0.5-1.0 grams/liter), coumarin (0.5 grams/liter), pH 2.0, temperature 55°C. The sodium lauryl sulfate acted as a surfactant, and the saccharin acted as a stress reliever to help produce fine grains. The anode was a nickel foil. High current densities of 0.1 to 0.2 A/cm², corresponding to a nickel deposition rate of 100-150 gm/hour, lowered the time required to electroplate the 490 μm tall nickel prototype structures to just four hours. Profilometric measurements of the heights of the structures indicated no more than a three μm variation in height across any one structure, and a variation not exceeding ten μm between any two structures, an acceptable range of variation. This modified Watts bath has two important advantages over the standard Watts bath in manufacturing mold inserts. First, high current densities can readily be achieved, on the order of 200 mA/cm², allowing the deposition of tall structures to be completed in a few hours. Conventional nickel plating procedures would require many hours or even days to electroplate such high structures. PMMA is hydrophilic and swells gradually in the presence of water. Stresses generated as PMMA swells in aqueous electrolytic baths could cause PMMA to delaminate from the substrate. Shorter electroplating runs help minimize this

An example is an article of manufacture comprising a heat sink to augment heat transfer between an object and the surroundings, wherein: (a) the object has a face whose surface area is at least about 1 cm²; (b) said heat sink comprises a plurality of at least about 100 microposts per cm² of surface area of the face, wherein each of said microposts has a distal end and a proximal end; (c) said proximal end of each of said microposts is connected to the face; (d) said distal end of each of said microposts is not connected to a shield, wall, or other object that inhibits heat transfer; and (e) the distance between the proximal and distal ends of each of said microposts is between about 0.05 mm and about 1.0 mm, and the aspect ratio of each of said microposts is at least about 5; whereby total heat transfer between the object and the surroundings is substantially greater than would be the heat transfer between an otherwise identical object lacking said microposts and the surroundings.

Preferably: (a) said heat sink comprises a plurality of at least about 1000 microstructures per cm² of surface area of the face; (b) the distance between the proximal and distal ends of each of said microposts is at least about 0.1 mm; and (c) each said micropost is farther from the nearest neighboring micropost than a distance of about 5 times the diameter of said micropost.

For example, consider an otherwise flat surface covered with nickel posts 20 μm in diameter and 800 μm long, with an air freestream velocity over the surface of 10 m/sec.

If the plate is flat, the heat transfer coefficient h is given by

$$h = .037 K/L (V_\infty L / \nu)^{0.8} Pr^{0.333}$$

Assuming that the fluid has the properties of air at room temperature, that the temperature of the plate is constant, T_o , and that the length of the plate is 1.0 m, then $h = 38 \text{ W/m}^2 \cdot ^\circ\text{K}$. The rate of heat transfer per unit area, q , is given by

$$q = (38 \text{ W/m}^2 \cdot ^\circ\text{K})(T_o - T_\infty)$$

where T_∞ is the freestream temperature.

Using published values for these properties of air, the value of h is calculated as 2820 W/m²-°K. Note that this value is two orders of magnitude higher than the convective heat transfer coefficient for the flat plate without microstructures.

The heat transfer flux through each post, assuming the thermal conductivity of the nickel post is 50 W/m-°K, is given by:

$$q = (168,000 \text{ W/m}^2\text{-}^\circ\text{K})(T_o - T_\infty)$$

Note that the heat transfer of a micropost is over four thousand times greater than the heat transfer of an area of flat sheet having the same size as the cross-section of the base of the post.

The overall heat transfer from a surface with microposts covering 2% of the surface area of the plate is the weighted average of the heat transfer rate from the 2% covered with posts and the 98% not covered with posts. Assuming that convective heat transfer between the area not covered with posts and the air is not substantially altered by the presence of the posts, the effective heat transfer coefficient between the surface and the air is (.02)(168,000) + (.98)(38) = 3397 W/m²-°K, an increase of almost two orders of magnitude compared to a flat plate of the same size. This calculated ratio is probably too high, because internal resistances in the plate will limit heat transfer through each post, but it is nevertheless true that HARM posts dramatically decrease thermal resistance between a surface and the surrounding medium. In cases where the convective heat transfer coefficient between a surface and the surrounding medium is a large contributor to the total resistance to heat transfer, adding HARMs to the surface can increase heat transfer dramatically.

Example 6: Composite Materials

In yet another application, HARMs can be used to join layers of dissimilar materials to form a composite material. HARMs can be used to bind materials together strongly that would otherwise bond weakly or not at all, allowing the production of novel composite materials. Weakness at the interface between different lamina in a laminated composite is often the limiting factor in controlling the properties of the laminate. Strong bonds between the lamina are usually desired. With prior technologies it has often been difficult to establish strong bonds between otherwise potentially useful material combinations. For example, metal-polymer and metal-

said microstructures is at least about 5; and (d) the shape of said proximal face of said second layer is substantially complementary to said microstructures; whereby the adhesion between said first and second layers is substantially greater than would be the adhesion between two otherwise identical layers lacking said microstructures.

Preferably: (a) said proximal face of said first layer is connected to the proximal ends of each of a plurality of at least about 100 microstructures per cm^2 of surface area of the proximal face of said first layer; (b) the distance between the proximal and distal ends of each of said microstructures is between about 0.1 mm and about 0.5 mm, and the aspect ratio of each of said microstructures is at least about 10; and (c) each of said microstructures is closer to the nearest neighboring microstructure than a distance of about 5 times the width of said microstructure.

Example 7: Acoustic absorbers

Yet another application of HARMs is as acoustic absorbers, to reduce the amplitude of sound transmitted through a surface. Sound waves impinging on one side of a surface cause the surface to vibrate; the vibrating surface then transmits sound energy to its surroundings on the opposite side; air is usually the medium of interest. The human ear can detect sound in an audible range from about 20 to about 15,000 Hertz. At a given frequency, the amplitude of sound increases with the amplitude of the vibration of the surface. Covering the surface with appropriate microstructures can reduce the amplitude of transmitted vibrations, and can therefore reduce the amplitude of the sound transmitted to the surrounding medium. The natural frequency of the microstructures is a function of their geometry and composition. The geometry and composition are chosen so that the natural frequency is below that of the vibrations of interest. They will thus oscillate out of phase with those vibrations, and the amplitude of the vibrations at the tips of the microstructures will therefore be less than the amplitude of the vibrations of the underlying surface. Because the amplitude of displacement of the tips of the microstructures is small, the sound transmitted across the surface is greatly reduced, because it is primarily at those tips where sound energy is transmitted to the adjacent air.

Consider, for example, two flat sheets, one without a layer of HARMs and one with a layer of HARMs to be described below. In both cases a forcing function on one side causes the sheets to vibrate at 5000 Hz. The sheet without microstructures will transmit sound of frequency 5000 Hz to the surrounding air at a particular amplitude.

reference in their entirety. In the event of an otherwise irresolvable conflict, however, the present specification shall control.

1 8. A process as recited in Claim 1, wherein the non-conductive sheet is a ceramic.

1 9. A metal surface with microstructures produced by the process of Claim 1.

1 10. A method for producing microstructures on a metal surface, comprising the steps
2 of:

3 (a) chemically bonding to the metal surface a polymer sheet; wherein there is no gap or
4 there is a negligible gap between the metal surface and the polymer sheet; wherein the
5 polymer sheet contains an exposed, developable, but undeveloped latent image of a
6 plurality of holes or structures; wherein the latent image is formed in the polymer sheet at
7 a time when the polymer sheet is not in contact with the metal surface;

8 (b) developing the latent image to produce a plurality of holes or structures in the polymer
9 sheet, without substantially affecting the chemical bonding between the metal surface and
10 the polymer sheet;

11 (c) removing the chemical bonding agent from the metal surface within the holes in the
12 polymer sheet, without substantially affecting the chemical bonding between the metal
13 surface and the undeveloped portions of the polymer sheet; and

14 (d) electroplating metal onto the metal surface within the holes of the polymer sheet;

15 whereby metal microstructures are produced on the metal surface.

1 11. A process as recited in Claim 10, wherein the metal surface is non-planar.

1 12. A process as recited in Claim 11, additionally comprising the step of heat-
2 shrinking the polymer sheet onto the metal surface.

1 **18.** A process as recited in Claim 17, wherein the metal surface is non-planar.

1 **19.** A process as recited in Claim 17, wherein the non-conductive sheet comprises a
2 polymer.

1 **20.** A process as recited in Claim 19, wherein said securing step comprises heat-
2 shrinking the polymer sheet onto the metal surface.

1 **21.** A process as recited in Claim 19, wherein the polymer sheet comprises poly
2 (methyl methacrylate).

1 **22.** A process as recited in Claim 17, wherein at least some of the holes in the non-
2 conductive sheet have an aspect ratio greater than about 5.

1 **23.** A process as recited in Claim 17, additionally comprising the step of removing the
2 non-conductive sheet from the metal surface after said electroplating step.

1 **24.** A process as recited in Claim 17, wherein the non-conductive sheet is a ceramic.

1 **25.** A process as recited in Claim 17, wherein the non-conductive sheet is formed by
2 molding.

1 **26.** A metal surface with microstructures produced by the process of Claim 17.

1 **27.** A non-conductive sheet having a plurality of holes, wherein:

2 (a) the sides of the holes are straight within a precision of $\pm 1 \mu\text{m}$;

3 (b) at least some of the holes have a non-circular cross-section;

4 (c) the size of at least some of the holes, in a direction parallel to the surface of the sheet,
5 is between about $1 \mu\text{m}$ and about $500 \mu\text{m}$.

- 4 (b) said heat barrier comprises a plurality of at least about 10 microstructures per cm²
5 of surface area of the first face;
- 6 (c) each of said microstructures comprises a shield and a post, wherein each of said
7 shields comprises a distal face and a proximal face, and wherein each of said posts
8 comprises a distal end and a proximal end;
- 9 (d) said distal end of said post of each of said microstructures is connected to said
10 proximal face of said shield of said microstructure;
- 11 (e) said proximal end of said post of each of said microstructures is connected to the
12 first face of the object;
- 13 (f) the surface area of the distal face of each of said shields is at least about 0.001
14 mm²; and
- 15 (g) the distance between the proximal face of each of said shields and the first face of
16 the object is between about 0.01 mm and about 2.0 mm;
- 17 whereby total heat transfer between the object and the surroundings is substantially less than
18 would be the heat transfer between an otherwise identical object lacking said heat barrier and the
19 surroundings.

1 42. An article of manufacture comprising a heat barrier to reduce heat transfer
2 between an object and the surroundings, wherein:

- 3 (a) the object has a first face whose surface area is at least about 10 cm²;
- 4 (b) said heat barrier comprises a substantially continuous layer that is substantially
5 parallel to said first face, and that is connected to said first face by a plurality of at least
6 about 10 microstructures per cm² of surface area of the first face;
- 7 (c) each of said microstructures comprises a distal end and a proximal end;
- 8 (d) said distal end of each of said microstructures is connected to said substantially
9 continuous layer;
- 10 (e) said proximal end of each of said microstructures is connected to the first face of
11 the object; and
- 12 (f) the distance between said substantially continuous layer and the first face of the
13 object is between about 0.01 mm and about 2.0 mm;

14 whereby total heat transfer between the object and the surroundings is substantially less than
15 would be the heat transfer between an otherwise identical object lacking said heat barrier and the
16 surroundings.

1 43.- An article of manufacture as recited in Claim 42, wherein the distance between
2 said substantially continuous layer and the first face of the object is between about 0.1 mm and
3 about 1.0 mm.

1 44. An article of manufacture as recited in Claim 42, wherein the object comprises a
2 turbine blade.

1 **48.** An article of manufacture as recited in Claim 47, wherein adjacent microstructures
2 are spaced between about 20 μm and about 50 μm apart from one another; wherein said wall is at
3 least about 0.5 mm tall in the direction perpendicular to said face; and wherein the height of said
4 microstructures is at least about 10 times the distance between adjacent microstructures.

1 **49.** An article of manufacture as recited in Claim 47, wherein the object comprises a
2 turbine blade.

1 51. An article of manufacture as recited in Claim 50, wherein:

2 (a) said heat sink comprises a plurality of at least about 10,000 microstructures per
3 cm² of surface area of the face;

4 (b) the distance between the proximal and distal ends of each of said microposts is at
5 least about 0.1 mm; and

6 (c) each said micropost is farther from the nearest neighboring micropost than a
7 distance of about 5 times the diameter of said micropost.

1 **53.** A composite material as recited in Claim 52, wherein:

2 (a) said proximal face of said first layer is connected to the proximal ends of each of
3 a plurality of at least about 100 microstructures per cm² of surface area of the proximal
4 face of said first layer;

5 (b) the distance between the proximal and distal ends of each of said microstructures
6 is between about 0.1 mm and about 0.5 mm, and the aspect ratio of each of said
7 microstructures is at least about 10; and

8 (c) each of said microstructures is closer to the nearest neighboring microstructure
9 than a distance of about 5 times the width of said microstructure.

1 **54.** A composite material as recited in Claim 52, wherein the shape of said
2 microstructures is such that said microstructures are physically interlocked securely with said
3 second layer, even disregarding any chemical bonding that may exist between said microstructures
4 and said second layer.

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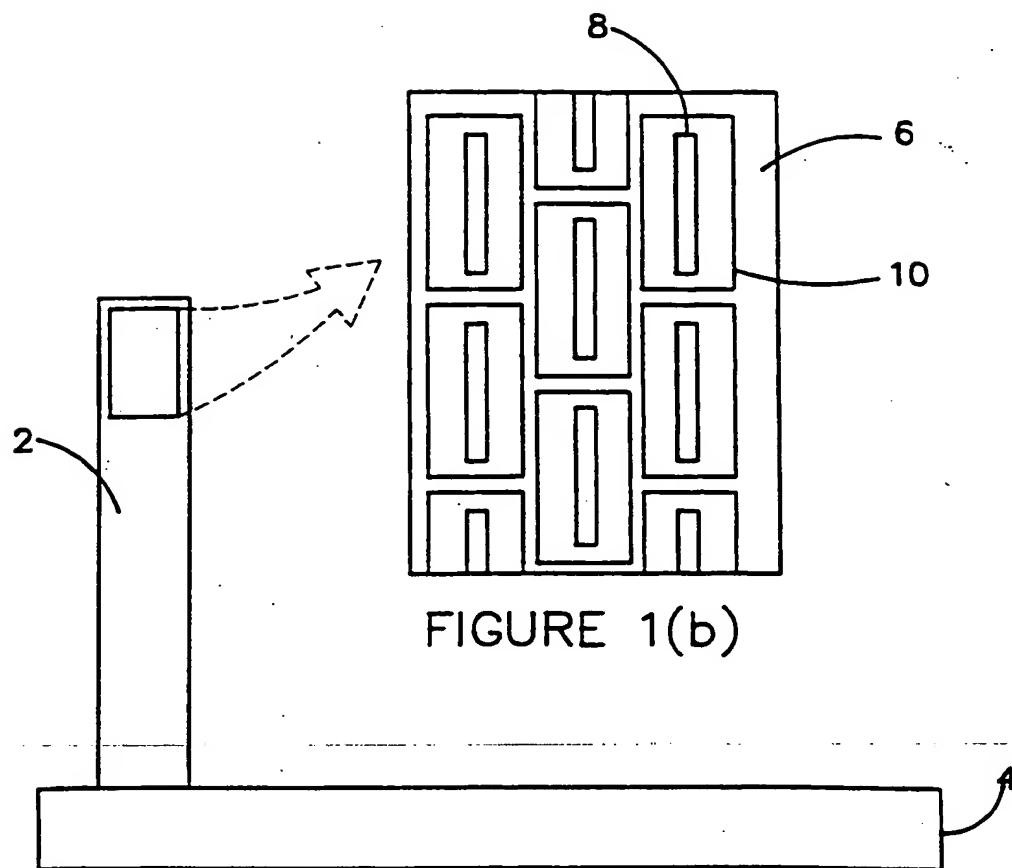


FIGURE 1(a)

FIGURE 1(b)

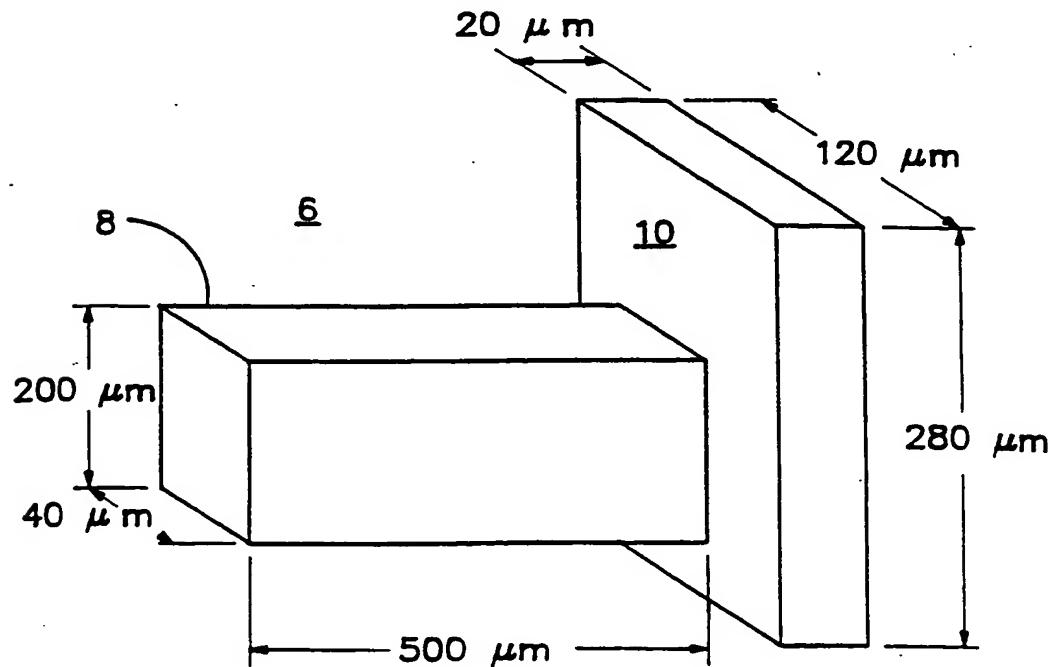


FIGURE 2

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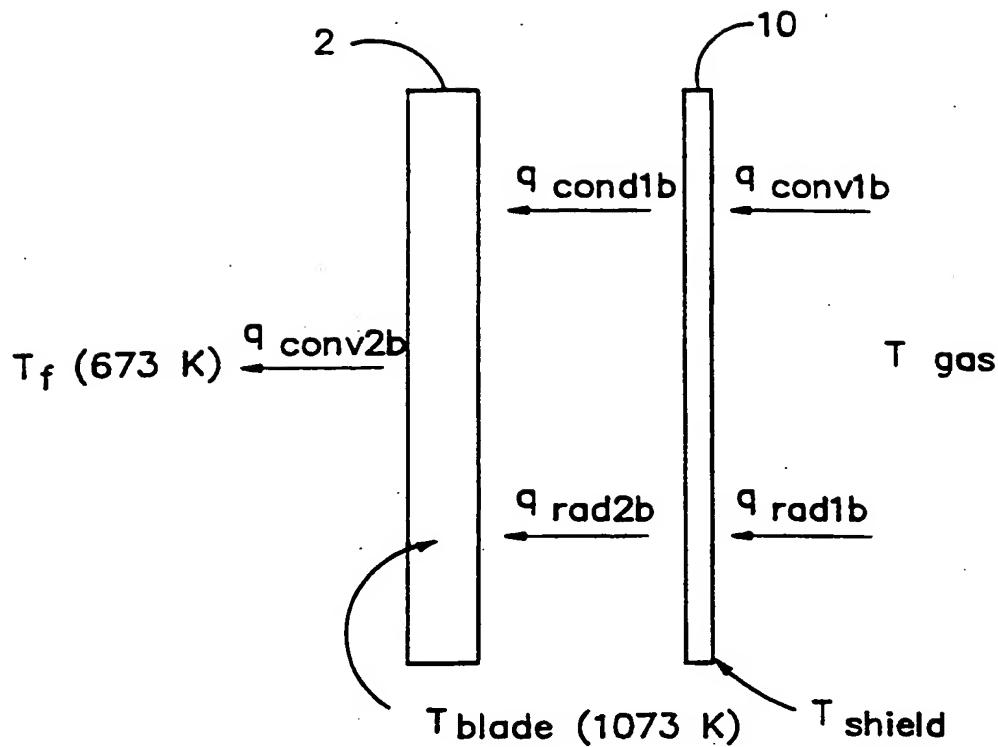


FIGURE 3(a)

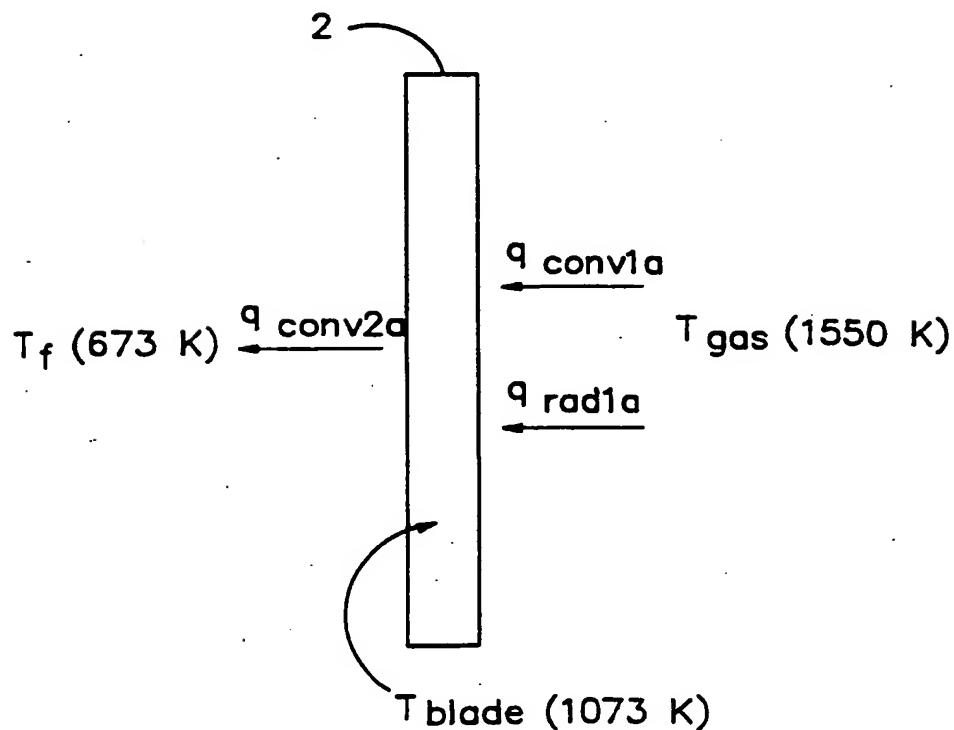
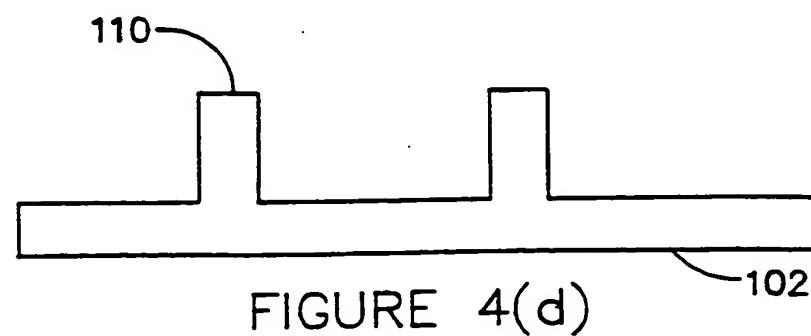
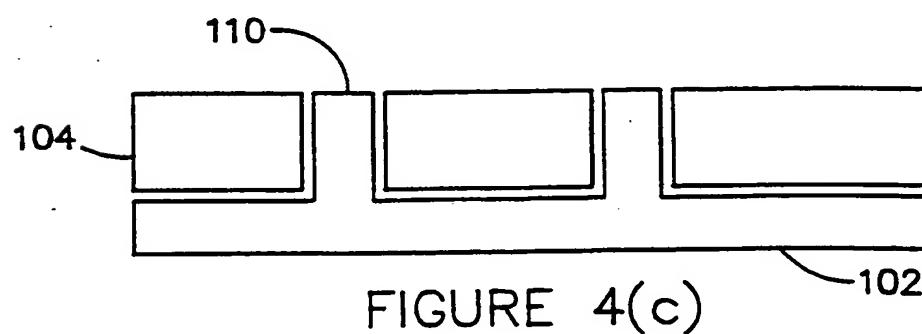
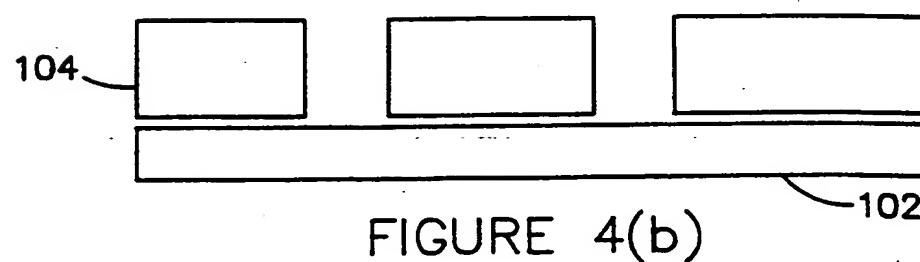
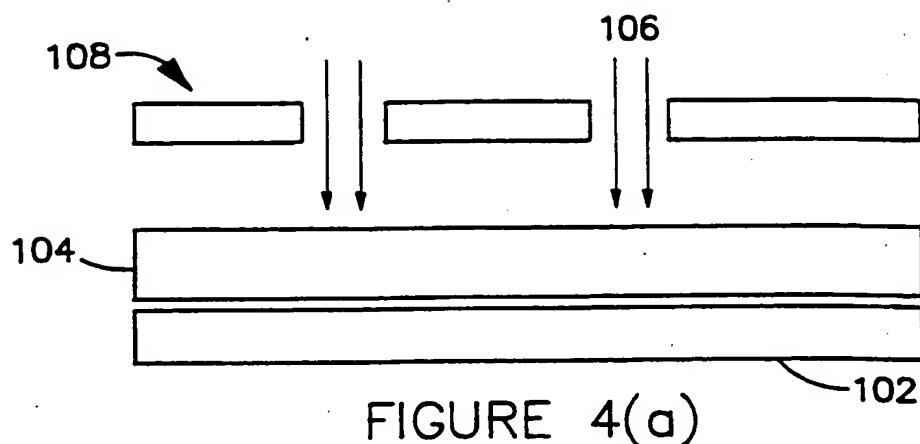
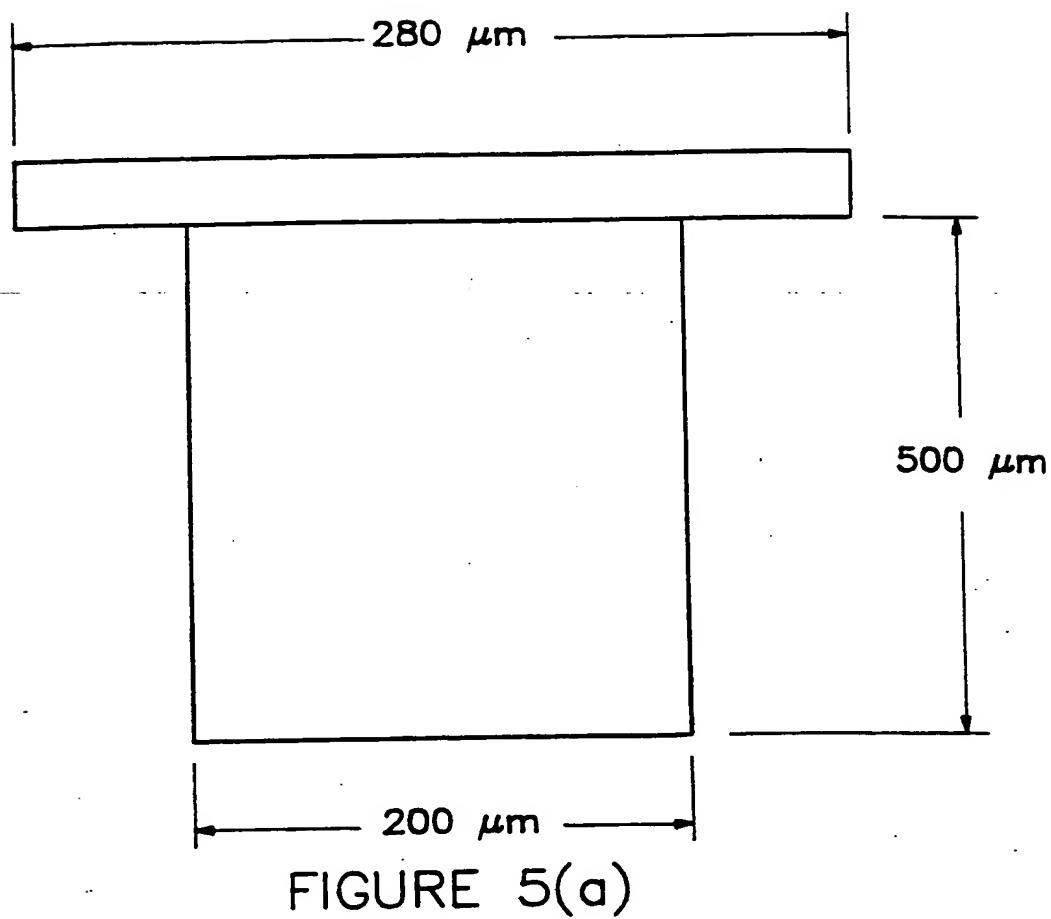


FIGURE 3(b)

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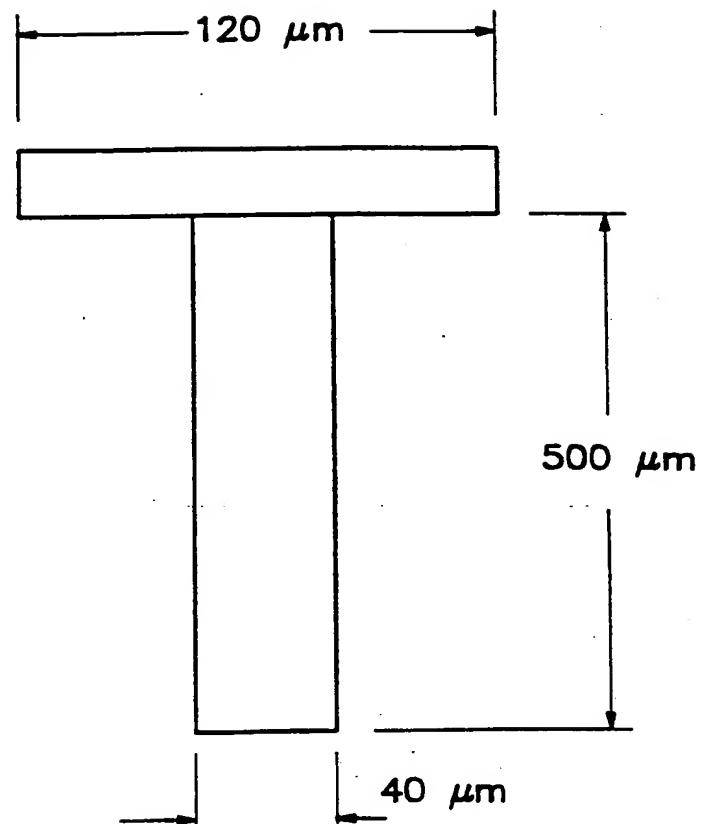


FIGURE 5(b)

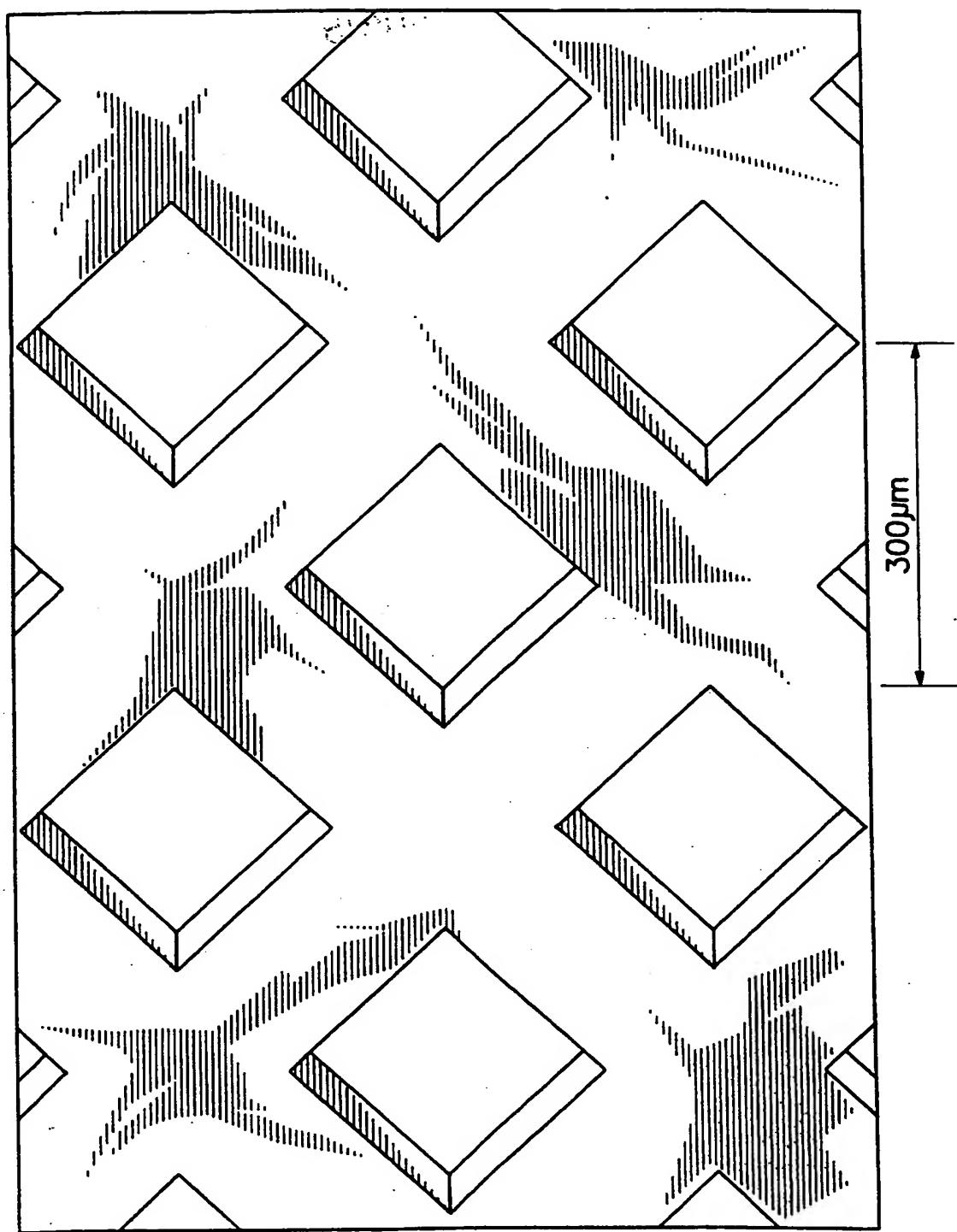
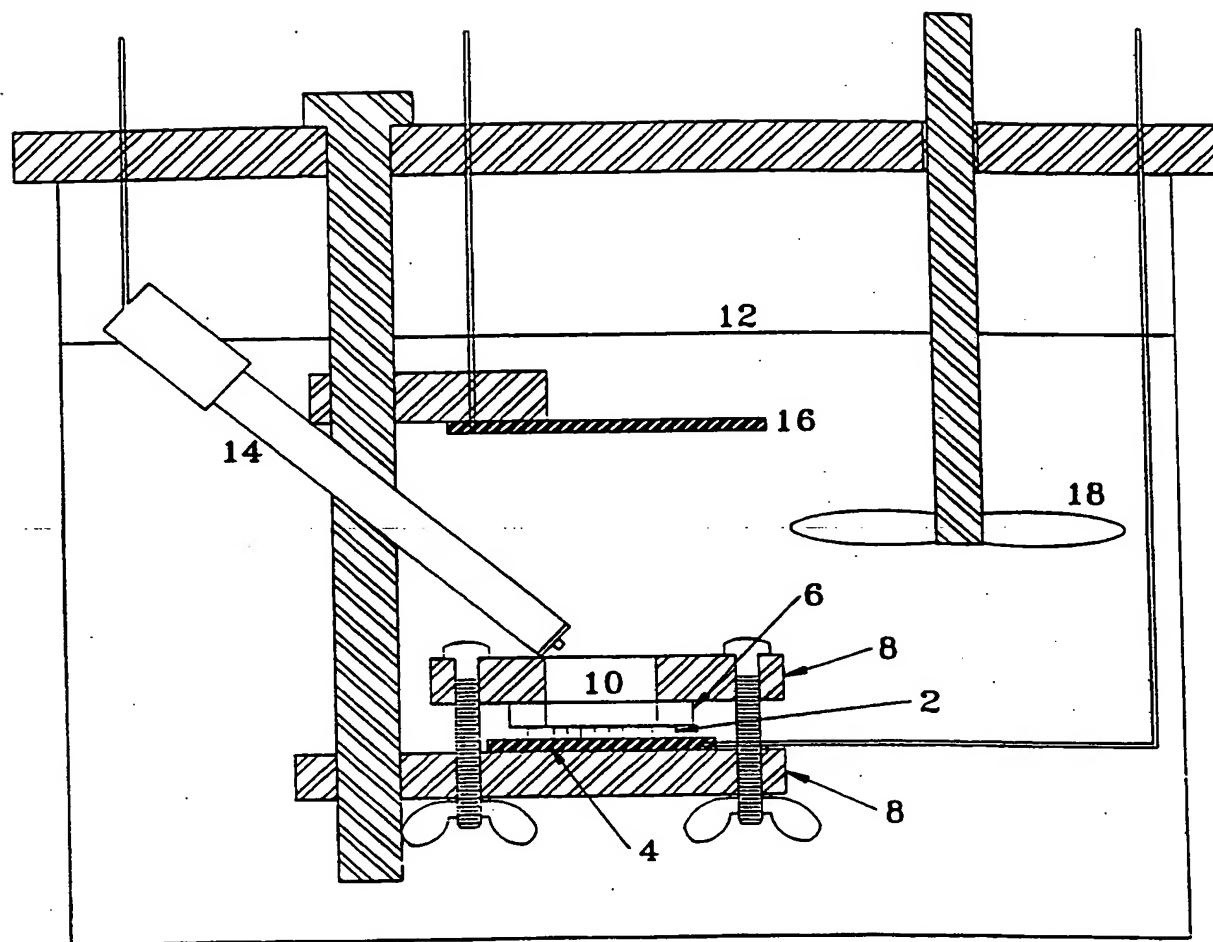


FIGURE 6

SUBSTITUTE SHEET (RULE 26)

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**FIGURE 7**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/01578

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C25D 5/02; G03C 5/00

US CL : 205/118, 135; 216/33, 39, 56; 430/324

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 205/118, 122, 135; 216/33, 39, 56; 430/324

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN, APS

search terms: microstructures, electroplating, developing, etching, bonding, resist, vias, holes, LIGA.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,728,231 A (GUREV) 17 April 1973 (17.04.73), col. 4, lines 3-27.	27-36
Y	US 5,045,439 A (MANER ET AL.) 03 September 1991 (03.09.91), col. 1, lines 8-11).	27
Y	US 5,378,583 A (GUCKEL ET AL.) 03 January 1995 (03.01.95), col. 11, line 15 to col. 12, line 25).	1-9
A	US 3,901,770 A (LITTWIN) 26 August 1975 (26.08.75).	
A	US 5,342,737 A (GEORGER, JR. ET AL.) 30 August 1994 (30.08.94).	

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	&	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
20 APRIL 1997	24 JUN 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer <i>M. Pendle Roy</i> for Kathryn Gorgos Telephone No. (703) 308-3328